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Dual fluorescence of naphthylamines in alkaline aqueous solution

Li-Hua Ma, Zhen-Chang Wen, Li-Rong Lin, Yun-Bao Jiang *

Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China

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Abstract

Dual fluorescence was observed with *N*-(1-naphthyl)aminoacetate (1-NAA) in aqueous solution of pH 13.0 in the presence of cationic surfactants, cetyltrimethylammonium bromide (CTAB) and chloride (CTAC), below and after the critical micelle concentration (CMC). Similar dual fluorescence was also found with 1- and 2-naphthylamine (1-NA, 2-NA), *N*-(2-naphthyl)aminoacetate (2-NAA) and (1-naphthyl)ethylenediamine (1-NEDA), in the presence and absence of the cationic surfactants, but not with *N*,*N*-disubstituted 1- and 2-NAs. We concluded that the dual fluorescence was due to the excited-state deprotonation of the amino group in these NAs. The pK_a^*s of the dual fluorescent NAs were estimated to be around 14 from the dual fluorescence pH titrations. No clear correlation was found for pK_a^* with the amino substitution and the presence of cationic micelle.

1. Introduction

The research on the acid–base equilibrium of naphthylamines (NAs) has mainly focused on the protonation at lower pH [1–3], whereas the acid dissociation of the NA has been limited. A possible reason could be the high ground-state pK_a of the amines, for example, the pK_a of NH_3 is 35 and of aniline is 25 [4]. Large differences in p*K* (often 6 units or more) of organic acids or bases have been observed upon excitation to the excited singlet state [5]. In the case of phenol and aniline [6,7], for example, it was reported that they were stronger acids in the excited state than in the ground state. Recent interest in the photophysics of NAs concerning the peculiar internal conversion character has shown that NAs have an emissive state of charge transfer character [8–11]. Enhancement in the acidity might be expected for NAs as 'acids', which would make it possible to observe the excited-state acid–base reaction. It is known that substitution at the reaction center, an electron-withdrawing group in particular [12], and the presence of cationic micelle [13] might enhance the ground-state proton dissociation reaction. Therefore we first prepared *N*-(1-naphthyl)aminoacetate (1-NAA, Scheme 1) that has an electron-withdrawing group substituted at the amino moiety and its carboxylic group could ensure a good binding to cationic micelle. We examined the fluorescence of 1-NAA in both cetyltrimethylammonium bromide (CTAB) and chloride (CTAC) solutions of varying pH and observed dual fluorescence at high pH. The investigations were then extended to other NA derivatives (Scheme 1) in order to clarify the origin of the dual fluorescence,

* Corresponding author. Fax: +86-592-218-5662.
E-mail address: ybjiang@xmu.edu.cn (Y.-B. Jiang).

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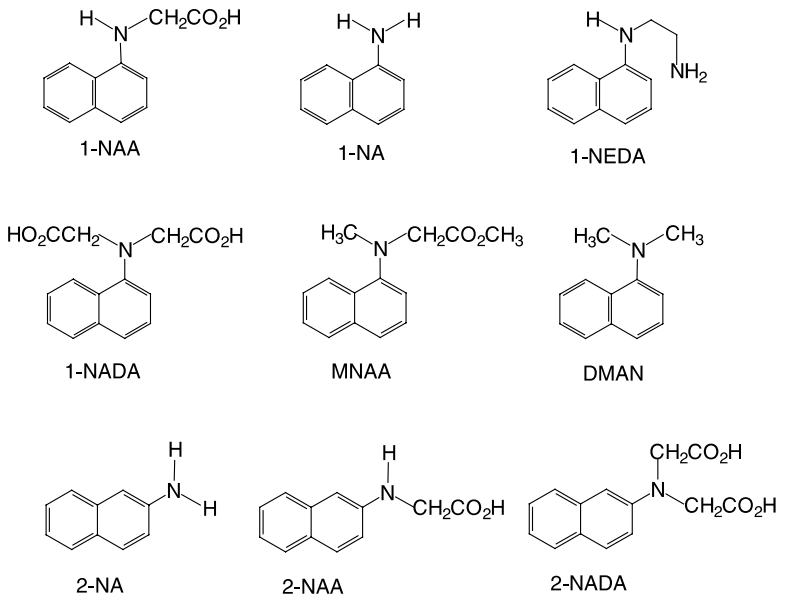

Scheme 1. Chemical structures of NAs and relative naphthalene derivatives.

which led to the conclusion that the dual fluorescence observed with NAs and its *N-mono*substituted derivatives was due to the excited-state acid–base reactions with the NAs as acids. The pK_a^*s were estimated and their relationship with molecular structure and the presence of cationic micelle were discussed.

2. Experimental

1-NAA was prepared by refluxing 1-naphthylamine (1-NA) and chloroacetic acid in aqueous sodium hydroxide solution [14]. The product was repeatedly recrystallized from absolute ethanol. ^{1}H NMR (DMSO-d^6, 500 MHz): δ 12.50(COOH–H), 8.122–8.106(1H, d), 7.779–7.762(1H, d), 7.449–7.421(2H, m), 7.279–7.248(1H, t), 7.146–7.130(1H, d), 6.352–6.337(1H, d), 3.979(2H, s), 3.348(s, N–H). *N*-(2-naphthyl)aminoacetate (2-NAA) was prepared by refluxing 2-naphthylamine (2-NA) with chloroacetic acid in a similar way and characterized by IR.

1-NADA was synthesized by further reaction of 1-NAA with chloroacetic acid. The product was subject to silica gel column chromatography eluting with absolute ethanol. ^{1}H NMR (D_2O, 500 MHz): δ 8.259–8.244(1H, d), 7.918–7.902(1H, d), 7.573–7.535(3H, m), 7.439–7.423(1H, t), 7.081–7.067(1H, d), 3.896(4H, s). 2-NADA was synthesized from 2-NAA and chloroacetic acid in a similar way and characterized by IR.

MNAA was prepared by methylization of 1-NAA by dimethyl sulfate at room temperature. The product was subject to silica gel column chromatography eluting with petroleum ether and ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.205–8.818 (1H, d), 7.788–7.772(1H, d), 7.513–7.329(4H, m), 7.329–7.132(1H, d), 3.886(2H, s), 3.683(3H, s), 2.980(3H, s).

DMAN was purchased from Fluka and purified by TLC prior to use. 1-NA, 2-NA, (1-naphthyl)ethylenediamine (1-NEDA) (AR, Shanghai), CTAB (AR, Shanghai) and CTAC (Tokyo Kasei) were used as received. Twice de-ionized water was further distilled in the presence of $KMnO_4$. The solution pH was adjusted by NaOH.

Corrected fluorescence emission and excitation spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer under excitation wavelength of 320 nm by a Xenon lamp of 150 W. Absorption spectra were taken on Beckman

DU-7400 absorption spectrophotometer using a 1-cm quartz cell. IR spectra were measured on Nicolet Avatar FT-IR 360 spectrophotometer. ^{1}H NMR spectra were measured on a Varian Unity$^+$ 500 MHz NMR spectrometer. All experiments were carried out at room temperature (25 ± 3 °C).

3. Results and discussion

3.1. Fluorescence spectra of 1-NAA

Fig. 1 shows the fluorescence spectra of 1-NAA in pH 13.0 alkaline solutions of varying CTAB concentration. In pH 13.0 aqueous solution without CTAB, 1-NAA emitted a single band fluorescence peaked at 447 nm. Upon addition of CTAB into the solution, the emission was quenched and blue-shifted, and a wide and structureless emission at longer wavelength of 545 nm appeared. The latter band did not shift as CTAB concentration was increased. The intensity ratio of the long-wavelength emission to the short-wavelength emission, I_{lw}/I_{sw}, was found to increase with increasing CTAB concentration before the critical micelle concentration (CMC) of CTAB (9.2×10^{-4} M) and level off after the CMC, which is clearly shown in the inset of Fig. 1. The excitation spectra obtained by monitoring emission at 425 and 545 nm, respectively, were similar, indicating that the 425 and 545 nm emission have the same excitation origin. This means that the emissive state for the 545 nm emission was generated from the emissive state for the 425 nm emission, and therefore the appearance of the dual fluorescence was due to an excited-state reaction. Similar observations were made for 1-NAA in alkaline CTAC solutions in which the intensity ratio was found higher than that in CTAB solution.

3.2. Origins for the dual fluorescence of 1-NAA

The observation of dual fluorescence for anionic fluorophore in the presence of a cationic surfactant, such as 4-(1-pyrene) butyric acid in CTAB or CTAC solution, has been reported and the dual fluorescence was ascribed to the excimer formation because of the aggregation of anionic fluorophores in aqueous solution induced by CTAB or CTAC [15,16]. The dual fluorescence of

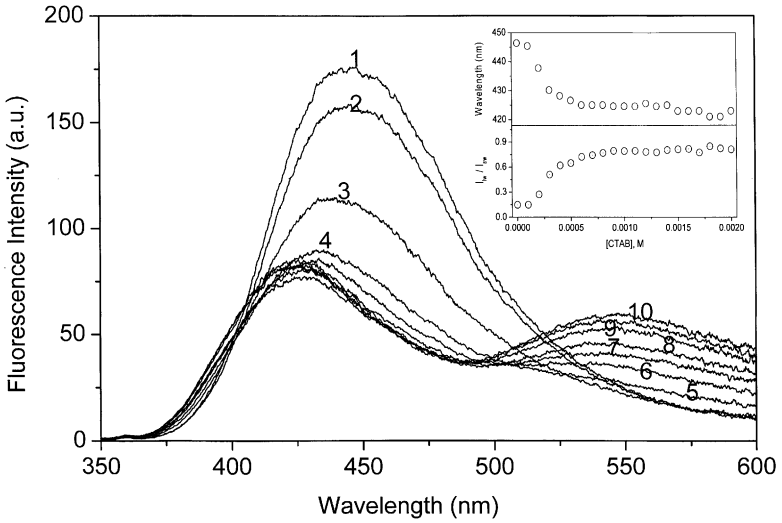

Fig. 1. Fluorescence spectra of 1-NAA in pH 13.0 aqueous solution as a function of CTAB concentration. Inset shows the variations of the short-wavelength band position and I_{lw}/I_{sw} of 1-NAA with CTAB concentration. 'lw' means long-wavelength and 'sw' means short-wavelength. [1-NAA] is 3.0×10^{-5} M. Curves 1–10 show the spectra with CTAB concentration varying from 0 to 1.5×10^{-3} M: (1) 0 M, (2) 1.0×10^{-4} M, (3) 2.0×10^{-4} M, (4) 3.0×10^{-4} M, (5) 4.0×10^{-4} M, (6) 5.0×10^{-4} M, (7) 6.0×10^{-4} M, (8) 8.0×10^{-4} M, (9) 1.0×10^{-3} M, and (10) 1.5×10^{-3} M.

1-NAA in alkaline CTAB solutions looked like the phenomenon mentioned above. We noted, however, that I_{lw}/I_{sw} increased with CTAB concentration below the CMC and leveled off beyond CMC (inset in Fig. 1), which is different from the 4-(1-pyrene) butyric acid/CTAB system in which the intensity ratio decreased at higher CTAB concentration [16]. Also, the intensity ratio was found, instead of increasing as expected from the excimer mechanism, to decrease with increasing 1-NAA concentration (Fig. 2). It thus appeared that the dual fluorescence observed with 1-NAA in CTAB and CTAC solutions was not due to excimer formation, though the aggregation of 1-NAA in the presence of CTAB was suggested by the appreciable red-shift in the absorption spectra (not shown). The fact that no dual fluorescence was found from similar series of solutions at pH 11–13, when 1-NAA existed in the anionic form [17] as at pH > 13, suggested that the observation of dual fluorescence at highly alkaline CTAB solution might relate to the excited-state acidic dissociation of the amine moiety in 1-NAA. Meanwhile, we indeed observed a continuous blue-shift of the 1-NAA fluorescence in ethanol–water mixtures of increasing ethanol content, which pointed to the charge transfer character of the emissive state [18]. An excited-state charge transfer promoted acidic dissociation reactions could then be assumed as the origin for dual emission. We thus extended our investigation to other 1-NA derivatives and 2-NA in the presence and absence of cationic surfactants. We found that these NA derivatives with at least one amino hydrogen, such as 1-NA, 1-NAA, 1-NEDA, 2-NA, 2-NAA (Scheme 1), showed dual fluorescence in highly alkaline solutions both in the presence and absence of CTAB or CTAC, see

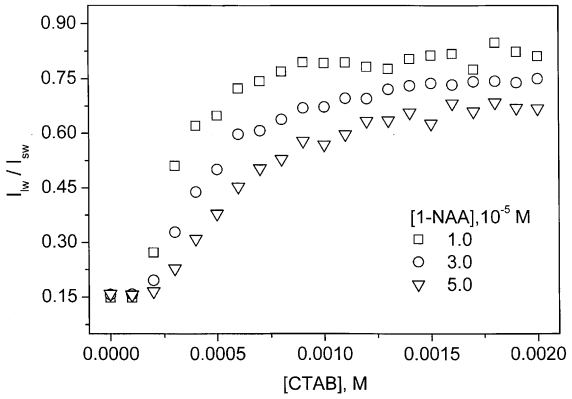

Fig. 2. The concentration effect on the intensity ratio of 1-NAA in pH 13.0 aqueous CTAB solutions.

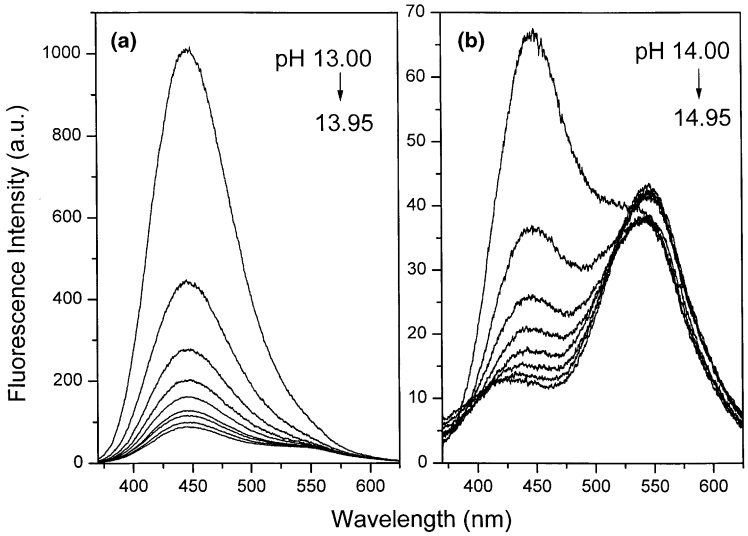

Fig. 3. Fluorescence spectra of 1-NA as a function of pH; [1-NA] is 1.0×10^{-5} M.

for example, in Fig. 3 the fluorescence spectra of 1-NA as a function of pH, whereas *N*,*N*-disubstituted NAs, such as 1-NADA, MNAA, 2-NADA and DMAN (Scheme 1), did not show dual fluorescence. It was therefore evident that the dual fluorescence observed with NAs in highly alkaline solution originated from the excited-state acid–base reaction, with the short-wavelength emission corresponding to the acid form of the amines while the long-wavelength emission to the dissociated 'base' amines. Table 1 compiled the detailed data for the emission band positions of both the acid and base forms of the investigated NAs.

3.3. pH titration of NAs' dual fluorescence

In order to evaluate the excited-state pK_a^*, the pH titrations of the dual fluorescence were carried out. Fig. 4 shows the intensity ratio, I_{lw}/I_{sw}, in the absence and presence of CTAB micelle, as a function of pH for the dual fluorescent NAs, from which pK_a^*s were estimated from the inflection points and tabulated together with those in CTAC micelle in Table 1. It was found that in the presence of CTAB or CTAC (not shown) micelle, the pH titration profiles were similar to those in the absence of micelle. Several significant features,

Table 1
The maximum emission wavelengths, intensity ratio of the long-wavelength to short-wavelength emission and the pK_a^*s of the dual fluorescent NAs in aqueous solution and in CTAB, CTAC micelles

NAs	Water				CTAB[a]				CTAC[a]			
	λ_1[b] (nm)	λ_2[c] (nm)	I_{lw}/I_{sw}[d]	pK_a^*	λ_1[b] (nm)	λ_2[c] (nm)	I_{lw}/I_{sw}[d]	pK_a^*	λ_1[b] (nm)	λ_2[c] (nm)	I_{lw}/I_{sw}[d]	pK_a^*
1-NA	545	447	3.18	14.6	545	414	22.0	14.2	547	420	79.0	14.3
1-NAA	545	447	0.99	14.7	545	425	1.56	14.7	545	423	1.72	14.2
1-NEDA	545	447	1.38	13.9	550	419	5.08	13.8	551	421	7.31	13.8
2-NA	535	410	2.99	13.7	528	404	4.56	13.6	533	420	13.6	13.7

[a] CTAB and CTAC concentrations are 1.5×10^{-3} M.
[b] Emission maximum of the base form.
[c] Emission maximum of the acid form.
[d] Taken at pH 14.5.

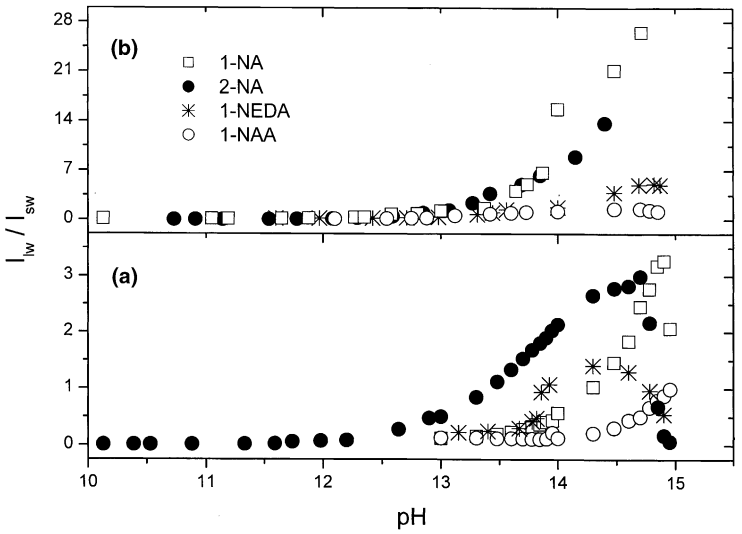

Fig. 4. pH titration curves for the dual fluorescent NAs in the absence (a) and presence (b) of 1.5×10^{-3} M CTAB.

however, deserved to be pointed out. In CTAB or CTAC micelle, the emission from the acid form is in general shifted to the blue, which is indicative of the charge transfer character of the emissive state, whereas the emission from the base form did not show appreciable spectral shift which means that the excited base form is of low dipole moment. The presence of CTAB or CTAC micelle decreased the minimum pH for observing the dual fluorescence, for example, in aqueous solution the minimum pH for observing 1-NAA dual fluorescence was 13.6 while in the presence of 1.0×10^{-3} M CTAB, this pH decreased to 13.0. The presence of CTAB or CTAC micelle also enhanced the base to acid emission intensity ratio (see Table 1), which could be due to the shift of excited-base equilibrium and/or the better protection of the excited base form.

The pK_a^* values presented in Table 1 showed that, within the experiment accuracy, the presence of CTAB or CTAC micelle did not change the pK_a^*, suggesting that the excited-state acid–base equilibrium was not affected by the micelle. This is in clear difference from that observed for ground-state pK_a [13]. It was hence assumed that the micelles provided better shielding of the base form that lead to higher intensity ratio in the micelle compared to that in aqueous solution. It was also noted from Table 1 that the pK_a^*s were around 14, both in aqueous solution and in micellar media, inspite of the different substituents at the amino group. This is quite different from the case in the ground-state acid–base dissociation, in which a decrease in pK_a could be observed when the acid center is substituted by an electron-withdrawing group, see for example, the variations of pK_a of *N*-substituted anilines [12].

We observed from the solvatochromic investigations that all the dual fluorescent NAs had a locally excited state of charge transfer character. The substitution of an electron-withdrawing group at the amino nitrogen would, on the one hand, enhance the acidic dissociation, whereas on the other hand suppress the electron transfer that would be unfavorable for the acidic dissociation. As a consequence, the charge transfer promoted excited-state acid–base equilibrium showed no clear correlation with the substitution at the reaction center. The weak relevance of the pK_a^*s to the cationic micelle could be analyzed similarly, since the cationic micelle could enhance the dissociation as observed for that in the ground state [13], but also suppress the charge transfer because of the less polar micellar environment.

4. Conclusions

We observed both in the presence and absence of CTAB and CTAC micelles in highly alkaline solutions the dual fluorescence of 1- and 2-NAs and their *N*-monosubstituted derivatives, but not with *N*,*N*-disubstituted derivatives. We concluded that the dual fluorescence was due to the excited-state acidic dissociation of these NAs, which is facilitated by the excited-state charge transfer. The pK_a^*s were estimated from the dual fluorescence pH titration curves as around 14 and showed no clear correlation with the substitution at the amino group and the presence of cationic micelles. We showed that the excited acid form of the dual fluorescent NAs had a dipole moment higher than that of the ground state, while that of the excited base form had a dipole moment similar to that of the ground state. This is, to the best of our knowledge, the first report to show the excited-state deprotonation of NAs and the emissions of the involved forms.

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